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Use of Pressure Equipment in Synthetic Organic Chemistry

By J. B. DICKEY*

In the past, many organic laboratories preferred not to undertake the synthesis of individual compounds or research programs if equipment operating in excess of several atmospheres' pressure was needed. In many instances, methods far more tedious and less direct were employed to make certain compounds than would have been necessary if suitable pressure equipment had been used. This tended to limit the programs in research laboratories and, in many cases, to increase the cost of those that were actually carried out.

In the past fifteen years, several firms** have designed and manufactured equipment suitable for working safely at pressures ranging up to 3000 atmospheres. Special equipment of small size is also supplied for pressure ranges considerably in excess of 3000 atmospheres. The equipment that is available is of the batch type. However, it is generally true that high-pressure equipment suitable for a continuous processing operation can be constructed to handle a process that has been worked out in batch-type equipment.

In the extensive literature dealing with the synthesis of organic compounds under pressure, noteworthy books have been written by Sabatier (*1*), Ellis (*2*), Marek and Hahn (*3*), Ipatieff (*4*), and Adkins (*5*). The technical literature dealing with the construction and use of pressure equipment is well covered by Tongue (*6*), Adkins (*5*), and by Gilson and Baskerville (*7*). For particular data as to the pressures of reaction, techniques of use, and care of equipment, attention is directed to Adkins (*5*).

The use of pressure equipment as an aid in the synthesis of organic compounds will be indicated by the reactions that are given on the pages that follow. All of the compounds listed can be prepared by the use of pressure equipment. The pressures which are required range between about 5 atmospheres and 400 atmospheres.

The use of high-pressure apparatus should not be regarded as the only procedure for making a particular compound. Alternative procedures should be given careful consideration. When using pressure equipment, the formation of the desired substance may be accompanied by the production of unwanted by-products. The reactions given on the remaining pages of this pamphlet are, however, suggestive of the wide variety of syntheses that can be carried out with such equipment.

*Research Laboratories, Eastman Kodak Company, Rochester, N. Y.

**Such as American Instrument Co., Silver Springs, Md., and Burgess-Parr Co., Freeport, Illinois.

I. Aromatic Ring Substitution with Ammonia or Derivative

A. Elimination of Hydroxyl

1. 2,4-Dinitro-α-naphthol + Ammonia $\xrightarrow{190°C\pm}$ 2,4-Dinitro-α-naphthylamine
2. Resorcinol + Ammonia $\xrightarrow[200°C\pm]{(NH_4Cl)}$ m-Aminophenol / m-Phenylenediamine
3. Leucoquinizarin + Ammonia $\xrightarrow{90°C\pm}$ *leuco*-1-Amino-4-hydroxyanthraquinone

   Leucoquinizarin + Ammonia $\xrightarrow{90°C\pm}$ *leuco*-1-,4-Diamino-anthraquinone
4. 1,5-Dihydroxynaphthalene + Ammonia $\xrightarrow{200°C\pm}$ 1-Amino-5-naphthol
5. Hydroquinone + Propylamine $\xrightarrow{200°C\pm}$ p-Propylaminophenol
6. Hydroquinone + Methylamine $\xrightarrow{200°C\pm}$ p-Methylaminophenol
7. Resorcinol + Dimethylamine $\xrightarrow[200°C\pm]{(CH_3)_2NH\cdot HCl}$ m-Dimethylaminophenol
8. 2-Hydroxy-3-naphthoic acid + Ammonia $\xrightarrow{260°C\pm}$ 2-Amino-3-naphthoic acid

B. Elimination of Halogen Atoms

1. Chlorobenzene + CH_3NH_2 $\xrightarrow[225°C\pm]{(Cu\ Cat.)}$ Methylaniline
2. p-Nitrochlorobenzene + Ammonia $\xrightarrow{180°C\pm}$ p-Nitro-aniline
3. 1,2-Difluoro-4-nitrobenzene + Ammonia $\xrightarrow{180°C\pm}$ 4-Nitro-2-fluoroaniline
4. p-Chloroacetophenone + Ammonia $\xrightarrow{195°C\pm}$ p-Amino-acetophenone
5. 2-Chloroanthraquinone + Ammonia $\xrightarrow{195°C\pm}$ 2-Amino-anthraquinone
6. o-Nitrochlorobenzene + β-Methoxyethylamine $\xrightarrow{100°C\pm}$ o-Nitro-β-methoxyethyl-aniline

C. Elimination of Sulfonic Acid and Nitro Groups

1. Sodium Anthraquinone-2-sulfonic acid + Ammonia $\xrightarrow{190°C\pm}$ 2-Aminoanthra-quinone
2. Sodium Anthraquinone-1-sulfonic acid + Methylamine $\xrightarrow{165°C\pm}$ 1-Methylamino-anthraquinone
3. 1,2-Dichloro-4,5-dinitrobenzene + Ammonia $\longrightarrow$ 1,2-Dichloro-4-nitro-5-ami-nobenzene
4. Sodium Anthraquinone-1-sulfonate + Lime and Water $\xrightarrow{190°C\pm}$ 1-Hydroxyan-thraquinone

II. Alkylamines Using Alcohol + $\begin{matrix} R \\ \diagdown \\ \quad NH \\ \diagup \\ R \end{matrix}$ + a Hydrogenation Catalyst

1. β-Methoxyethanol + Ammonia $\xrightarrow[225°C\pm]{(Ni)}$ β-Methoxyethylamine

2. Diethylenetriamine $\xrightarrow[225°C\pm]{(Ni)}$ Piperazine

3. Tetrahydrofurfuryl Alcohol + Ammonia $\xrightarrow[225°C\pm]{(Ni)}$ Tetrahydrofurfurylamine

4. Aniline + Ethanol $\xrightarrow[225°C\pm]{(Ni)}$ Ethylaniline

5. Decanediol-1,10 + Ammonia $\xrightarrow[225°C\pm]{(Ni)}$ 1,10-Diamino Decane

6. Ethylamine $\xrightarrow[225°C\pm]{(Ni)}$ Diethylamine + Ammonia

The very important reaction (1-5 inclusive) was discovered by Ernst and Mack, and is covered by U. S. Patent 1,982,985 (1934).

III. Reductions Carried Out Under Pressure, Giving an Organic Base

1. Furfuraldoxime $\xrightarrow[75°C\pm]{(Ni)}$ Furfurylamine

2. Nitroethane $\xrightarrow[25°C\pm]{(Ni)}$ Ethylamine

3. Acetaldehyde Ammonia $\xrightarrow[25°C\pm]{(Ni)}$ Ethylamine

4. Acetone + Ammonia $\xrightarrow[50°C\pm]{(Ni)}$ Iso-Propylamine

5. Benzalaniline $\xrightarrow[50°C\pm]{(Ni)}$ Benzylaniline

6. 2,4-Dinitroaniline $\xrightarrow[25°C\pm]{(Ni)}$ m-Phenylenediamine

7. o-Nitrophenol $\xrightarrow[50°C\pm]{(Ni)}$ o-Aminophenol

8. Nitroquinoline $\xrightarrow[25°C\pm]{(Ni)}$ 5-Aminoquinoline

9. o-Nitrophenoxyacetone $\xrightarrow[75°C\pm]{(Ni)}$ 2-Methylphenomorpholine

10. p-Nitrosodiethylaniline $\xrightarrow[50°C\pm]{(Ni)}$ p-Aminodiethylaniline

11. Adiponitrile $\xrightarrow[100°C\pm]{(Ni)\ (NH_3)}$ Hexamethylenediamine

12. m-Nitrobenzaldimethylal $\xrightarrow[130°C\pm]{(Ni)}$ m-Toluidine

IV. Reduction of Ring Systems

1. Furfural $\xrightarrow[100°C\pm]{(Ni)}$ Tetrahydrofurfuryl Alcohol
2. Aniline $\xrightarrow[200°C\pm]{(Ni)}$ Cyclohexylamine
3. Quinoline $\xrightarrow[75°C\pm]{(Ni)}$ Tetrahydroquinoline
4. Pyridine $\xrightarrow[150°C\pm]{(Ni)}$ Piperidine
5. Resorcinol in alkali $\xrightarrow[90°C\pm]{(Ni)}$ Dihydroresorcinol

V. Miscellaneous Reactions Carried Out Under Pressure

1. Sodium Ricinoleate + NaOH $\longrightarrow$ Sebacic Acid
2. Acetonitrile + H_2S $\longrightarrow$ Thioacetamide
3. Hydroquinone + Diethyl Sulfate $\xrightarrow[NaOH]{150°C\pm}$ Hydroquinonediethyl Ether
4. Aniline + Ethylene Oxide $\xrightarrow{130°C\pm}$ β-Hydroxyethyl and Di-β-Hydroxyethylaniline
5. Aniline + Methanol $\xrightarrow[200°C\pm]{H_2SO_4}$ Methyl and Dimethylaniline
6. Tetrahydrofurfuryl Acetate + Acetic Anhydride $\xrightarrow[225°C\pm]{ZnCl_2}$ Pentane Trioltriacetate
7. Ethylene + Vinyl Acetate $\xrightarrow[(0)1000\ At+]{180°C\pm}$ Resin
8. Ethanol + Carbon Monoxide $\xrightarrow[700\ At]{(BF_3)\ (150°C\pm)}$ Propionic Acid

References

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(*6*) Tongue, "The Design and Construction of High Pressure Chemical Plant," D. Van Nostrand Company, New York (1934).

(*7*) Gilson and Baskerville, *Chemistry in Industry*, *62*, 450 (1943) "A General Purpose Laboratory Autoclave."